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**Title:** Synthesis and Characterization of Heterobenzenacyclo-octaphanes Derived from Cyclotetrabenzoin

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Synthesis and Characterization of Heterobenzenacyclooctaphanes Derived from Cyclotetrabenzoin


Abstract: We describe the modular synthesis and characterization of several substituted N-hetero benzenacyclooctaphanes (BAOs), a new motif for heteroaromatic conjugated macrocycles. The targets were synthesized via condensation of substituted aromatic ortho-diamines with a cyclic octaketone building block in moderate to excellent yields (41–91%). We evaluated the optical and electronic properties and the solid-state structures of the targets and discuss their properties through comparison with their linear diphenyl N-heteroacene counterparts.

Introduction

Design and syntheses of π-conjugated cyclic macroolecules,[1] such as macrocyclic annulenes and benzoannulenes,[2] have received significant attention. Other notable members of this broad class of molecules are cyclic oligophenylene, conjugated strings of benzene rings cyclized via para- (CPPs),[3] ortho- (COPs) and meta- (CMPS)[4] positions, with size dependent electronic and optical properties. Closely related to them are N-hetero benzenacyclooctaphanes (BAOs) first synthesized by Endo and Suzuki en route to [8]circulenes.[5] BAOs combine para- and meta-connections on benzenoid rings within one circle. While these representatives have a pure carbon backbone, the self-assembling cyclic 2,5-connected oligothiophenes or porphyrin nanorings are examples for heteroaromatic cycles.[6] Expanding this concept, the group of Nuckolls developed specialized, soluble heteroaromatic chiral conjugated macrocycles with alternating donor bithiophene and acceptor perylene dimide subunits.[7] CPPs, BAOs and chiral conjugated macrocycles were synthesized by Pd-catalyzed couplings using modular building blocks.[3,5] The couplings have to overcome a large steric strain in the final cyclization steps which impedes high yields and thus hinders large scale applications. The cyclisation has to be improved[9] or carried out at the very beginning of the synthesis to avoid loss of complex building blocks and allow the introduction of further functionalities.[9] Herein, we report a convenient route to heteroaromatic cyclic conjugated molecules, enhancing the BAO motif. We use our reported benzoin ring-forming reaction of terephthalaldehyde to cyclotetrabenzoin 1 (Scheme 1, bottom) to get access to the cyclic octaketone building block 2.[10] The cyclisation takes place at the beginning and utilizes cheap building blocks and catalysts. A neat access to several structural motifs is provided, using condensations of derivatives such as (TIPS)-ethynylated ortho-diamines.[11] Linear N-heteroacenes with their electron accepting properties are attractive materials in the field of organic electronics.[12] Constructing cyclic structures from these azaacene building blocks gives rise to novel electronic properties resulting from the enlarged, cyclic conjugated systems with N-heteroacene subunits. Stabilizing and solubilizing side groups turn the presented compounds into easy-to-handle macrocycles.[13] In this work we present the synthesis of substituted N-hetero benzenacyclooctaphanes (BAOs) and investigate the structural, optical and electronic properties.

Previous work

![Scheme 1. Synthesis of benzoctabenzenacyclooctaphanes by Suzuki et al. and the benzoin condensation yielding cyclotetrabenzoin 1.[3,10]](image-url)

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Scheme 2. Synthesis of cyclotetra[benzil] 2 and subsequent condensations to the N-Hetero-benzenacyclooctaphanes 4a–5h. A more detailed scheme with all structures is shown in the SI.

Results and Discussion

We have recently reported the synthesis of cyclotetra[benzoin] 1. Its oxidation yields octaketone 2, which we dubbed “cyclotetra[benzil]” in 76% yield (Scheme 2). The parent quinoxaline macrocycle 4a was prepared in 84% yield in a condensation of 2 with four equivalents of the ortho-phenylenediamine (3a); similar reaction conditions allowed the preparation of 4b–d in good to high yields. [Tris(isopropl/isilyl)-ethynyl-substituted precursor ortho-diamines 3e–h improved the solubility in derivatives 4e–h, which were obtained using AcOH in CHCl3. Yields range from 41 to 80%. Surprisingly, with 3h the twofold condensed tetraketone 5h was isolated in 50% yield. Compound 5h offered the possibility for the synthesis of mixed condensation products such as 5i (Scheme 2), which was formed in 78% yield by a condensation with diamine 3f. Using PhMe as the solvent instead of CHCl3 allowed the formation of 4h in 52% yield. To elucidate the effect of cyclization on their properties, a cyclic model compounds 7e–h were prepared through condensation of the ortho-diamines 3a–d with benxil 6 (Scheme 3). The condensation of 2 with chiral diamines 8a–b to derivatives 9a–b proceeded in high yields, indicating that the introduction of saturated functionalities is also possible.

Figure 1. Photographs of 4e–f, 4h, 7e–f and 7h under UV light with illumination at 365 nm (left) in n-hexane and in daylight (right).
Table 1. Spectroscopic and electrochemical properties of 4a–h, 5h–l and 7e–h. A full table with of all compounds is shown in the SI.

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<th>Compd.</th>
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<th>(\lambda_{\text{onset}}) [nm]</th>
<th>(\lambda_{\text{max, em.}}) [nm]</th>
<th>(\varepsilon) [L/(mol*cm)]</th>
<th>(E_{\text{HOMO}}) [eV]</th>
<th>(E_{\text{LUMO}}) [eV]</th>
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UV-Vis measurements for 4e–g, 5h–l were performed in \(n\)-hexane; 4a, in CH\(_2\)Cl\(_2\). \(^{*}\)First reduction potentials measured by cyclic voltammetry (CV) in THF with Bu\(_4\)NPF\(_6\) as the electrolyte against Fc/Fc\(^{+}\) as an internal standard (~4.80 eV) at 200 mV/s. \(^{*}\)HOMO = \(E_{\text{LUMO}}\,\text{CV} - \Delta E_{\text{UV}}\). \(^{*}\)Calculated from CV measurements (\(E_{\text{LUMO CV}} = -4.80\) eV \(-\Delta E_{\text{CV}}\)). \(^{*}\)Calculated from \(\lambda_{\text{onset}}\) in \(n\)-hexane for 4e–g and 5h–l and in CH\(_2\)Cl\(_2\) for 2, 4a–d, 5a. \(^{*}\)Quantum yields as solutions in \(n\)-hexane or CH\(_2\)Cl\(_2\) from average values of three independent measurement.

Figure 2 Different views of single crystal structures of 5a, 4a, 4e and 4f (from left to right); the TIPS-ethynyl groups of 4e–f are shown as thin lines.
A significant redshift in the UV-vis spectra is observed by increasing the size of the heteroacene appendix from quinoxaline 4e to diazaanthracene 4f and to dian-6,9-hexaazaazatetracenes, 4g-h and 5i. The longer azaacene systems 4f-h and 7e-h show a characteristic fine structure at longer wavelengths. Figure 3 shows a comparison of a tetraazaazacene backbone as a macrocycle 4h and its linear counterpart 7h. The shape of the different absorption spectra is largely determined by the acene subunit. In addition to the absorption maxima of the acene appendix, a strong absorption between 310–370 nm for 4h and 5i is observed and it seems that cyclisation increases the absorptivity between 400 and 500 nm, which could be useful for advanced optoelectronic applications like Organic Photovoltaics (OPVs). We also observed a small red shift for the macrocycles (9 nm going from 7h to 4h), which is observed in all comparisons of cyclic to linear counterparts (4e-h vs. 7e-h, see Supporting Information). A comparison of 4h with the mixed compound 5i shows, that the shape of the UV-Vis spectrum of 5i is quite similar to that of 4h, the λmax,abs 595 nm and λmax,ext 616 nm values are even identical. From the UV-Vis (λmax) and cyclic voltammetry (CV) measurements, the ionization potentials, HOMO/LUMO energy levels and optical bandgaps were estimated (Table 1). For the TIPS ethynylated compounds 4e-g the gap decreases by enlarging the azaacene subunit: it shifts from 2.99 eV for 4e, to 2.42 eV for 4f and finally to 2.07 eV for 4g. The gaps of the non-cyclic analogues 7e-g are subtly increased. Compounds 4a-h, 5h-i and 7e-h display one pseudoreversible reduction peak E(0/−) and no oxidation peak. The measurements show, that the electrochemical and optical properties are determined by the choice of corresponding ortho-diamines and a plethora of further different structure motifs as cyclic molecules is available through our building block 2.

X-Ray measurements and 1H NMR experiments disclose the cyclic structures. Diffraction-quality single crystals of 4a-f, 5a, 7e-f and 7h were grown by vapour diffusion methods (see SI). Progressing from 5a to 4a-f increases the number of rigidifying fusions around the central cavity, which results in first elongating for 5a, and later by twisting the macrocycle into saddle-shaped structures of 4a-f. By introducing the bulky TIPS-ethyl groups of 4e-f, solvents are intercalated (about 6.3 molecules of PhMe for each molecule of 4e and about 5.5 molecules of CHCl3 for each molecule of 4f), resulting in a reduced quality of the structure. The 1H NMR signals of the hydrogens of the central ring in 4e-h are broad singlets, while 4a—without bulky groups—shows a sharp singlet, which suggests that the phenylene groups in the central ring of 4a have more freedom for rotation (see SI). Figure 4 depicts this effect for 4e and 4g in detail. By cooling 4e to −40°C, the phenylene protons behave differently, showing two broad singlets. Increasing up to room temperature counteracts this effect, and one broad singlet is observed.

**Conclusion**

In conclusion, we developed a new and highly modular synthetic strategy to access a class of conjugated functionalized heteroaromatic cyclic molecules, by doing the yield-limiting cyclization step at the beginning of the synthesis. Through various halogenated, unsaturated and TIPS-ethynylated ortho-diamines the effect of incorporating different motifs into the cyclic backbone were examined. The optical and electronic properties are primarily determined by the linear azaacenene subunit; however, a small bathochromic shift compared to the linear counterparts is observed. In the future, we are going to investigate their unique physical properties. The increased absorptivity by the cyclisation combined with a high solubility could be applied in many areas of organic electronics such as for organic photovoltaics (OPV). Furthermore, mixed heterocycles like 5i could prove to be exciting candidates for novel donor/acceptor systems.

**Experimental Section**

**Materials and Methods**
All reagents and solvents were obtained from commercial suppliers and were used without further purification. For chromatography, the 40–60 °C petrol ether fraction was used. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of nitrogen by using Schlenk techniques. For column chromatographic purifications a manual column chromatography (SiO₂, grain size 0.04 – 0.063 mm) was used. ¹H (270 °C) NMR-spectra were recorded on 300 MHz (75 MHz), 400 MHz (100 MHz), 500 MHz (125 MHz) or 600 MHz (150 MHz) spectrometers. The ¹³C NMR signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C atom (positive signal), – = secondary C atom (negative signal), and Cq = quaternary C atom (no signal). Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of [¹H] solvent in the corresponding deuterated solvent. Mass spectra were recorded using high resolution direct analysis in real time (HR-DART) or high resolution matrix desorption/ionization (HR-MALDI) detected by magnetic sector FT-ICR (Fourier transform ion cyclotron resonance) techniques. Infrared (IR) spectra are reported as solid phase measurement in wavenumbers (cm⁻¹). Samples were taken under daylight or illumination at 365 nm. Quantum yields Φ were obtained by the absolute method using an Ulbricht sphere. Given Φ for solutions in n-hexane are average values of three independent measurements for solutions. The CV experiments were carried out using a glassy carbon working electrode, a platinum/titanium wire auxiliary electrode, a silver wire reference electrode, a 0.1 M NBU₄PF₆ solution in degassed dry tetrahydrofuran, and ferrocene/ferrocenium as the reference redox system and internal standard (~4.8 eV). To determine the first reduction potentials (E(0/−)) and the first oxidation potential of ferrocene, the half-wave potentials were used.

**Syntheses**

(3R,6S,9R,12S)-3,6,9,12-tetrahydroxy-1,4,7,10(1,4)-tetrabenzenacyclododecaphe-2,5,8,11-tetraene (1), 3,6-bis[(trisopropylsilyl)ethyl]benzene-1,2-diamine (3e), 1,4-bis[(trisopropylsilyl)ethyl]naphthalene-2,3-diamine (3f), 1,4-bis[(trisopropylsilyl)ethyl]anthracene-2,3-diamine (3g), and 1,4-bis[(trisopropylsilyl)ethyl]phenazine-2,3-diamine (3h) were synthesized according to literature procedures.

**General Procedure 1 (GP1).**

A solution of the 1,4,7,10(1,4)-tetrabenzenacyclododecaphe-2,5,8,9,11,12-octacne 2 (1.00 equiv.), ortho-diamine 3a-d or 8a-b (4.00 equiv.) and α,ω-PhMesulfonyl acid (2.00 equiv.) in EtOH (40 mL) was prepared in a round bottom flask fitted with a Dean-Stark condenser. The solution was heated to reflux for 2 d at 120 °C under stirring. The mixture was cooled to room temperature, filtered, and washed with EtOH (30 mL), and Et₂O (30 mL), respectively. After filtration, the product was recrystallized from CHCl₃/EtOH to afford pure product (if needed). The suitable single crystals were obtained using slow vapor diffusion of different solvents into the CHCl₃ or dichloroethane solution of product.

**General Procedure 2 (GP2).**

A solution of the 1,4,7,10(1,4)-tetrabenzenacyclododecaphe-2,3,5,6,8,9,11,12-octacne 2 (1.00 equiv.) and the ortho-diamine 3e-h (4.05 equiv.) in a 1:1 mixture of CHCl₃ and AcOH was prepared in a round bottom flask fitted with a condenser. The solution was heated to reflux for 5 d at 80 °C under stirring. The mixture was cooled to room temperature and carefully diluted with a saturated aqueous solution of sodium hydrogen carbonate (1.00 mL). The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic phases were washed with water (50 mL) followed by brine (50 mL) and then dried over magnesium sulfate. After filtration, the solvent was evaporated, and the crude solid was purified by column chromatography (silicon dioxide; petroleum ether/CH₂Cl₂ 10:1) and crystallized (EtOH/CH₂Cl₂ 10:1).

The suitable single crystals were obtained using slow vapor diffusion of n-hexane into the CHCl₃ solution of product. Yield: 351 mg, 64%, 4,5,9,10-tetrabenzenaacyclooctaphane (decomposition).

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Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4c)
The GP1 was applied to 2 (528 mg, 1.00 mmol, 1.00 equiv.), 4-difluoro-1,2-phenylenediamine 3c (1.58 g, 4.00 mmol, 4 equiv.), and p-toluenesulfonic acid (380 mg, 0.20 mmol, 0.20 equiv.) in EtOH (40 mL) yielded a grey solid. Yield: 868 mg, 66.51%. Mp: ≥ 400°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 76.04, H 8.67, N 4.54. Calcld. for C_{661,644}H_{588,544}O_{444}: C 76.04, H 8.67, N 4.54.

Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4d)
The GP1 was applied to 2 (528 mg, 0.10 mmol, 1.00 equiv.), 4-fluoro-1,2-phenylenediamine 3d (50.5 mg, 0.40 mmol, 4 equiv.), and p-toluenesulfonic acid (3.80 mg, 0.02 mmol, 0.20 equiv.) in EtOH (4 mL) yielded a pale-grey solid. Yield: 73 mg, 92.89%. Mp: ≥ 400°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 76.54, H 6.81, N 7.09. Calcld. for C_{661,644}H_{588,544}O_{444}: C 76.54, H 6.81, N 7.09.

Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4e)
The GP2 was applied to 2 (350 mg, 0.50 mmol, 1.00 equiv.) and 2 (252 mg, 476 µmol, 1.00 equiv.) in dichloromethane (10 mL) and AcOH (10 mL). Flash column chromatography and crystallization (EtOH/EtOAc 100:1, 50 mL) yielded a colorless solid. Yield: 186 mg, 83.21%. Mp: 160.1°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09. Calcld. for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09.

Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4f)
The GP2 was applied to 2 (11.00 g, 21.93 mmol, 4.05 equiv.) and 2 (252 mg, 476 µmol, 1.00 equiv.) in dichloromethane (10 mL) and AcOH (10 mL). Flash column chromatography and crystallization (EtOH/EtOAc 100:1, 20 mL) yielded a yellow crystalline solid. Yield: 936 mg, 381 µmol, 80%. Mp: 160.1°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09. Calcld. for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09.

Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4g)
The GP2 was applied to 2 (350 mg, 0.50 mmol, 1.00 equiv.) and 2 (252 mg, 476 µmol, 1.00 equiv.) in dichloromethane (10 mL) and AcOH (10 mL). Flash column chromatography and crystallization (EtOH/EtOAc 100:1, 20 mL) yielded a dark green solid. Yield: 237 mg, 89.0 µmol, 41%. Mp: 160.1°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09. Calcld. for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09.

Octafouro-2,4,6,8(2,3)-tetraquinoxalino-1,3,5,7(1,4)-tetrabenazaenacyclooctaphane (4h)
The GP2 was applied to 2 (350 mg, 0.50 mmol, 1.00 equiv.) and 2 (252 mg, 476 µmol, 1.00 equiv.) in dichloromethane (10 mL) and AcOH (10 mL). Flash column chromatography and crystallization (EtOH/EtOAc 100:1, 20 mL) yielded a dark green solid. Yield: 237 mg, 89.0 µmol, 41%. Mp: 160.1°C (decomposition). Elemental analysis calcd. (%) for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09. Calcld. for C_{661,644}H_{588,544}O_{444}: C 75.15, H 6.81, N 7.09.
The GP1 was applied to \(3a\) (100 mg, 193 \(\mu\)mol, 1.00 equiv.) and \(6\) (53.8 mg, 256 \(\mu\)mol, 1.20 equiv.) in chloroform (7 \(\mu\)L) and acetonitrile (2 \(\mu\)L) for 4 h at 90°C. Flash column chromatography and crystallization (silicon dioxide; petroleum ether/dichloromethane 1:1, v/v) yielded a red solid. Yield: 111 mg, 173 \(\mu\)mol, 81%. IR: \(\nu = 3058, 3027, 2966, 2870, 2861, 2830, 2761, 1719, 1565, 1351, 1249, 1136, 1018, 865, 841, 756 \text{ cm}^{-1}\). HRMS (direct analysis in real time, DART\(^+\)): \([M+H]^+\) calcd. for \(\text{C}_{468}\text{H}_{529}\text{N}_{20}\text{S}_{12}\): m/z 643.3898, found m/z 643.3902 correct isotope distribution. Elemental analysis calcd. (%) for \(\text{C}_{468}\text{H}_{529}\text{N}_{20}\text{S}_{12}: C 79.71, H 8.14, N 3.80.\)

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Keywords: azaacenes • tri-conjugated cycle • cyclophane • condensation • N-heterocycles


Different N. heterobenzenacyclooctaphanes were obtained by condensations with an octaketone building. We evaluated the optical and electronic properties of the targets and discuss their properties through comparison with their linear diphenyl N-heteroacene counterparts.